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(54) Color-developing plated metal for spring and the method of using the same.

(57) Disclosed is a color-developing metal product for spring plated on the surface with alternate layers of Cu and Zn to be alloyed by thermal diffusion at low temperatures after spring-forming, and a method of using a color-developing plated metal products comprising the steps of :
applying two-layer plating of a lower layer of Cu and an upper layer of Zn on the surface of a spring material to the extent that the thickness ratio of a Zn layer to the whole thickness of the plating is within the range from 5 to 45 % ; forming the plated spring steel material into a spring material having a final plating thickness of 2-25μm and spring-forming it; heating the spring-formed spring material at 250-400°C for low temperature annealing thereby alloying the plating layer to be colored.

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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to color-developing plated metal for spring and the method of using the same, and more specifically, to a color-developing plated metal for spring capable of being suitably distinguished in size, material and the like and the method of using the same.

Description of the Prior Art

A product formed of spring steel (that is, a spring) such as a coil spring or a sheet spring is used in various applications such as mechanical parts, official materials and daily necessaries. The spring steel as a material for the above spring includes a spring steel wire and a spring steel sheet. As the spring steel wire, there are known a hard drawn steel wire, a piano wire and a spring stainless steel wire specified in Japanese Industrial Standard (hereinafter referred to as JIS).

These steel wires resemble in the surface color tone with each other, and particularly, the hard drawn steel wire cannot be distinguished from the piano wire by only the color tone. Also, in the case of the stainless steel wire, it generally is more lustrous as compared with the hard drawn steel wire and the piano wire; however, when being finished by oil drawing (wet drawing), it cannot be distinguished by the color tone. Accordingly, of these steel wires after spring-forming, those resembling in size with each other have often suffered such a trouble that, there arises mixing in size or material, and consequently, the defective spring product is liable to be erroneously assembled in a mechanical structure.

Meanwhile, a steel cord for reinforcing a radial tire of an automobile is formed as follows: namely, five elementary wires each having a diameter of, for example, 0.25mm are stranded, and the stranded wire is knitted in a belt-shape and is disposed around the periphery of the tire. Thus, the steel cord aims at reinforcement of the radial tire as a rubber-metal cord composite material.

The above elementary wire is manufactured by the steps of: applying a Cu-plating as a lower layer and a Zn-plating as an upper layer on the surface of a raw wire having a diameter of 1.3mm at the plating thickness ratio of Cu:Zn = 7:3; heating the plated wire at approximately 400 C for a few minutes to tens of minutes for alloying the plating layers into a Cu-30%Zn alloy; and forcibly drawing it at a reduction ratio of 96.3% to a diameter of 0. 25mm. During such processes, after heating, the color of the plating surface is changed from white to gold, which exhibits a very beautiful color tone.

In the manufacture of the steel wire mentioned above, the fact that the surface color tone of the cord is changed to gold is worthless, and the object is to improve the drawability and adhesiveness between rubber and metal by alloying the plating layer into a Cu-30%Zn alloy. According ly, it has never been revealed to make positively function the coloring generated by plating the material with two different metals and applying the thermal diffusion thereto.

In addition, the steel coated with only a plating layer of Cu-30%Zn alloy has no problem in terms of the corrosion resistance when it is embedded in rubber, for example, as in the case of the steel cord and thus shielded from the outside air. However, in the case of using the above steel as a formed product without shielding it from the outside air, it is insufficient for the corrosion resistance and causes practically some problems.

To prevent from mixing of the above products formed of spring steel in size and material and also to improve the beautiful appearance, there have been executed the following coatings on the spring steel wire: various resin film coatings; baked coatings of paint; ion plating by PVD or CVD; and TiN coating.

However, in spring-forming, the spring steel wire is subjected to severe abrasion close to galling in passing through the forming tool , and is also subjected to a heat treatment (low temperature annealing) at 250 °C-400 °C for 2-10 min. after spring-forming for improving the spring characteristics. Consequently, the spring steel wire applied with a resin film or baking paint is liable to yield damage on the surface thereof during the spring-forming thereby causing peeling of the film, and also to be softened in film during the low temperature annealing thus causing depression in the film and mutual adhesion of the springs. The spring steel wire applied with ion plating does not bring the above problems; but has a disadvantage of increasing a cost. Therefore, in the existing conditions, any technique does not exhibit the sufficient function.

SUMMARY OF THE INVENTION

Taking the above circumstance into consideration, the present invention has been made, and an object is to facilitate the distinction among the spring steel

products and to improve the surface appearance, and further to improve the corrosion resistance by utilizing the conventional manufacturing technique for steel cords mentioned above.

To achieve the above object, the present inventors has earnestly studied, and found the fact that the plating does not significantly deteriorate the spring characteristic of the spring steel material and improves the corrosion resistance, and further causes the plating layer to be colored during the low temperature annealing after the spring-forming, and therefore, by suitable selection of the color tone of the spring steel product, it is possible to perform the distinction thereof in size and material.

In a first aspect of the present invention, there is provided coated metal for a spring having alternate plating layers of Cu and Zn on the surface thereof, which are alloyed in a low temperature thermal diffusion after the spring-forming on the surface thereof.

In a second aspect of the present invention, there is provided a method of using the said plated metal for a spring comprising the steps of: applying plating of alternate layers of Cu and Zn with a thickness ratio of the Zn layer to the whole thickness of the plating layers at 5-45% on the surface of a spring steel wire; adjusting the final plating thickness at 2 - 25μm, and spring-forming it; and heating the formed product at 250 -400 °C (low temperature annealing), thereby coloring the plating layer thereof.

In a third aspect of the present invention, there is provided plated metal for a spring having a Ni-plating layer on the surface thereof and subsequent alternate layers of Cu and Zn to be alloyed in a low temperature thermal diffusion after the spring-forming.

In a fourth aspect of the present invention, there is provided a method of using the said coated metal for a spring comprising the steps of: applying three-layer plating of a Ni-layer as a lower layer, a Cu-layer as an intermediate layer and a Zn-layer as an upper layer adjusting a thickness ratio of the Zn layer to the total thickness of the Cu-layer and Zn layer at 5-45% on the surface of a spring steel wire; adjusting the Ni-layer thickness and the total thickness of Cu-layer and Zn layer at 2-30μm and 2-25μm respectively, and spring-forming it; and heating the formed product at 250 - 400 °C (low temperature annealing), thereby coloring the plating layer thereof.

Prior to description of the preferred embodiments, there will be described the function of the present invention.

A Cu-Zn alloy plating layer alloyed by heating of two-layer plating of Cu-Zn can exhibit various color tones according to the heating conditions and the content of Zn, which makes easy the distinction thereof.

Further, as for a three-layer plating of a lower Ni-layer , an intermediate Cu-layer, and an upper Zn-layer, when it is heated at a relatively low temperature so as not to yield mutual diffusion between the lower Ni-layer and the intermediate Cu-layer, the intermediate Cu-layer and the upper Zn-alloy are alloyed by the mutual diffusion, to thus form a Cu-Zn alloy plating layer.

This can exhibit various color tones according to the heating conditions and the content of Zn, thus making easy the distinction thereof.

The present invention is intended to prevent the mixing of the products formed of spring steel different in size and material by utilizing the difference in the color tone of the color developing plating layer, and to improve the corrosion resistance by the Cu-Zn alloy plating layer and Ni-plating layer as a lower layer. However, if the characteristic of the product formed of spring steel is significantly deteriorated in use by the presence of the color-developing plating layer for distinction, it cannot be put to practical use. Accordingly, the color-developing plating layer is naturally specified in the optimal condition. Also, the Ni-plating layer as a lower layer is specified in the optimal condition. The present invention has been completed as a result of close investigation of the optimal conditions in the viewpoint of the distinction among products, the spring characteristic and corrosion resistance. Hereinafter, this will be concretely described with reference to the accompanying drawings.

A hard drawn steel wire is applied with two-layer plating (lower layer: Cu, upper layer: Zn) at a ratio of the thickness of the upper Zn-layer to the whole plating thickness of 30%, and is drawn and formed to coil spring. The formed hard drawn steel wire is heated in various conditions of temperatures and times and is then examined for change in color tone of the plating surface, which gives the results as shown in Fig. 1.

Further, a hard drawn steel wire is applied with three-layer plating (lower layer: Ni, intermediate layer: Cu, upper layer: Zn) at a ratio of the thickness of the Zn-layer to the total plating thickness of the Cu-layer and the Zn-layer of 30%, and is drawn and formed to coil spring. The formed hard drawn steel wire is heated in the same conditions as those in the above case applied with the two-layer plating and is then examined for change in color tone of the plating surface, which gives the same results as shown in Fig. 1.

The change in the color tone is closely dependent on the heating temperature and the heating time. There almost instantaneously occurs the color change from white to gold capable of being distinguished by the naked eye under the following condition: in the temperature range of the practical low temperature annealing (250 - 400 °C), when being at 250 °C, the heating time is 4 min. or more, and when being at

400°C, the heating time is 2 min. or more. As a result of such experiments, the heating time (t) required for generating the above color change in a temperature T (°C) within the range of 250 - 400°C is expressed as the following equation (1).

$$\log t \geq 1.193 - 2.386 \times 10^{-3} T \qquad (1)$$

Further, the hard drawn steel wire is applied with the same two-layer plating as the above at various plating thicknesses, and is drawn and spring-formed in the same manner as the above. The resultant hard drawn steel wire is then heated at 400°C for 5 min. or more to form a Cu-Zn alloy plating layer, which gives the relationship between the content of Zn(%) in the alloy and the color tone as shown in Fig. 2.

Also, the hard drawn steel wire is applied with the same three-layer plating as the above at various plating thicknesses, and is drawn and spring-formed in the same manner as the above. The resultant hard drawn steel wire is then heated at 400°C for 5 min. or more for alloying Cu in the intermediate layer and Zn in the upper layer by mutual diffusion to thus form a Cu-Zn alloy plating layer, which gives the same relationship as that in the case applied with the two-layer plating.

Referring to Fig. 2, in the range of 10- 45% of Zn, there appears the beautiful color tone of gold adapted to perform the function of distinction for preventing the mixing of the different materials, and which also significantly improve the surface appearance. Further, in the range of 5 - 10% Zn, there appears the color tone strongly affected by the color of Cu (red copper color) of a plating component, which is apparently different from the color of white (color of Zn) of the as-plated surface, and consequently, the spring thus treated is sufficiently distinguished from the ordinary spring having the surface colored in white (color of metal) thus being put in practical use.

Incidentally, one of the important properties of the product formed of spring steel lies in the corrosion resistance.

From the viewpoint of this, the spring applied with the same two-layer plating as shown in Fig. 2 is examined, which gives a relationship between the Zn (%) in a Cu-Zn alloy plating layer and the rusting time (corrosion reaching time up to the material) by a salt spray test using a solution containing 3% salt. The results are shown in Fig. 3. It is revealed from this figure that at the plating layer thickness of 2µm or more, the corrosion resistance is improved with increase in Zn content (%), and at the Zn content of 5-45%, the rusting time is made longer as compared with the non-plated hard drawn steel wire. Namely, it is apparent that the presence of the plating layer does not deteriorate the characteristic of the spring material but preferably improve it. At the plating layer thickness of 1µm, the plating layer is affected by the irregularities of surface of the spring material, thus exerting no effect on improvement of the corrosion resistance. In addition, in the case of using the a SUS 304 stainless steel wire in place of the hard steel drawn wire as a spring wire, the rusting time is obtained by adding the value as shown in Fig. 3 to the rusting time (185 hrs.) of the SUS 304 stainless steel spring itself.

Further, the spring coated with the same three-layer plating as the above is examined, which gives a relationship between the Zn (%) in a Cu-Zn alloy plating layer and the rusting time (corrosion reaching time up to the material) on the different thicknesses of the alloy plating layer and the lower Ni-layer, by a salt spray test using a solution containing 3% salt. The results are shown in Fig. 3. It is revealed from this figure that the corrosion resistance is improved by the presence of the Cu-Zn alloy plating layer and the lower Ni-plating layer. As for the Cu-Zn alloy plating layer, the rusting time is made longer with increase in Zn content thus improving the corrosion resistance. In particular, at the Zn content of 10% or more, the corrosion resistance is preferably improved, and the thickness thereof is preferably 2µm or more. As for the lower Ni-plating layer, the thickness thereof is preferably 2µm or more. In the case of the Cu-Zn alloy plating layer of 1 m and the lower Ni-plating layer of 1µm, the plating layer is affected by the irregularities of surface of the spring material which makes smaller the effect of improving the corrosion resistance. Preferably, each thickness of the Cu-Zn alloy plating layer and the lower Ni-layer is 2µm or more.

The corrosion resistance is enhanced with increase in each thickness. However, when the thicknesses of the Cu-Zn alloy plating layer and the Ni-plating layer exceed 25µm and 30µm, respectively, the corrosion resistance is not enhanced in proportion to increase in the thicknesses. Accordingly, in the viewpoint of the economy, the thicknesses of the Cu-Zn alloy plating layer and the Ni-plating layer are respectively 25µm or less and 30 µm or less respectively.

Next, hard drawn steel wire material of 3.5mm is applied with two-layer plating of Cu-Zn and is drawn at a reduction ratio of 91.7% to a diameter of 1mmϕ, after which it is heated at 400°C for 5 min. to be thus alloyed.

Similarly, a stainless steel wire material of 2.5mmϕ is applied with two-layer plating and is drawn at a reduction ratio of 84% to a diameter of 1mmϕ, after which it is heated at the same condition as the above,

to be thus alloyed. Fig. 4 shows a relationship between the Hunter's rotational bending fatigue strength and Zn content(%) with respect to the above wire materials. The hard drawn steel wire and the stainless steel wire are not reduced in fatigue strength at the plating layer thickness of 25μm or less; however, they are apparently reduced in fatigue strength at the plating layer thickness of 30μm. Accordingly, in practical use, the plating thickness is, preferably, less than 30μm. The same is true for the coil spring (spring steel product).

The above data is obtained for the spring steel material being as a wire and the product formed of spring steel being as a coil spring; however, the data is almost similar to that in the case of the spring steel material being as a sheet and the product formed of spring steel being as a sheet spring.

In summary, in the two-layer plating of Cu-Zn for the product formed of the spring steel , the following condition is preferable: the Cu-Zn alloy composition is within a range of 5-45%Zn in the viewpoint of the color tone effect; the plating thickness is 2μm or more in the viewpoint of the corrosion resistance, and is 25μm or less in the viewpoint of preventing reduction in fatigue strength; and the low temperature annealing condition for coloring is 250 • C × 4min. or more to 400 • C × 2min. or more.

Further, in the three-layer plating (lower layer: Ni, intermediate layer: Cu, upper layer: Zn) for the product formed of spring steel , the thickness of the lower Ni-layer is preferably 2μm or more in the viewpoint of the corrosion resistance, and 30μm or less in the viewpoint of economy. In a color Cu-Zn alloy plating layer, the following condition is preferable: the Cu-Zn alloy composition is within a range of 10-45%Zn in viewpoint of the color tone effect; the plating thickness is 2μm or more in the viewpoint of the corrosion resistance, and is 25μm or less in the viewpoint of economy; and the low temperature annealing condition for coloring is 250 • C × 4min. or more to 400 • C × 2min. or more.

The color developing coated metal for spring and the method of using the same according to the present invention is made in consideration of the above condition. Accordingly, it is possible to achieve the color tone effect of the color Cu-Zn alloy plating layer without deteriorating the spring characteristic thereby facilitating the distinction among spring steel formed products, and also to improve the surface appearance. Further, it is possible to improve the corrosion resistance by the Cu-Zn alloy plating layer and the lower Ni-plating layer.

In addition, the method of using coated metal according to the present invention has made to satisfy the above condition and comprises the steps of: applying two-layer plating (lower layer: Cu, upper layer: Zn) or three-layer plating (lower layer: Ni, intermediate layer: Cu, upper layer: Zn) on the surface of the spring steel material; spring-forming it; heating the formed steel at 250 - 400 • C (low temperature annealing) thereby making the plating layer being colored, to thus obtain the color -developing coated metal according to the present invention. However, the color-developing coated metal for spring may be obtained by the other methods. For example, there is considered a method comprising the steps of: heating the above spring material at 250 - 400 • C for making the plating layer colored, and then spring-forming it, followed by annealing; but this method makes the manufacturing processes complex because of adding one process, that is, the heating process. Consequently, in the present method, the plating layer is colored by the low temperature annealing indispensable after the spring-forming process, and therefore, the present invention is simple in the manufacturing processes and hence is excellent in economy.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view for explaining a relationship between the heating time and temperature, and color tone change in a Cu-Zn plating layer of a spring formed product;
Fig. 2 is a view for explaining a relationship between the Zn content and the color tone in a Cu-Zn plating layer of a spring formed product;
Fig. 3 is a view for explaining a relationship between the Zn content , and the rusting time in a Cu-Zn plating layer of a spring formed product concerning different plating layer thickness; and
Fig. 4 is a view for explaining a relationship between the Zn content and the Hunter's rotational fatigue strength in a Cu-Zn plating layer of a spring formed product concerning different plating layer thickness.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the exemplary embodiments will be described with reference to the accompanying drawings.

Example 1

A hard drawn steel wire containing 0.82% C was subjected to lead patenting, pickling and descaling to thus form a raw wire of 3.5mm ϕ. The raw wire was applied with two-layer plating of a low layer of Cu and a upper layer of Zn using a two-bath continuous electro-plating bath. In this case, Cu plating was applied under the following conditions: bath composition is $CuSO_4$:130g/l and 62%H_2SO_4: 33cc/l solution; pH is 1.5; temperature is 30 °C ; plating current density is 5A/dm^2 ; and anode is Cu plate. Zn plating was applied under the following condition: bath composition is $ZnSO_4 \cdot 7H_2O$: 410g/l, $AlCl_3 \cdot H_2O$: 20g/l, and Na_2SO_4: 75g/l solution; pH is 4; current density is 5A/dm^2; and anode is Zn plate. The plating times were set at the five kinds for changing the Zn thickness ratio to the whole thickness: namely, 0, 5, 30, 45, and 50%. At the same time, the whole plating thickness was adjusted to become 2μm, 25μm and 30μm after drawing.

After being applied with two-layer plating, the raw wire was drawn 8 times in the usual manner at a reduction ratio of 91.7% to a diameter of 1mm ϕ, to thus obtain an elementary wire within a strength level equivalent to 1mm ϕ of JIS 3521 hard drawn steel wire SWC.

The elementary wire of 1mm ϕ was formed into tight springs having an outside diameter of 10mm, length of 20mm and a number of winding of 20. Each tight spring was heated under a condition of 150 °C x 7 min., 200 °C x 5 min., 250 °C x 4 min., 300 °C x 3.5 min., and 400 °C x 2 min., which was examined for the colored state. Each tight spring after being heated was cooled and was examined for corrosion resistance by a salt spray test. Also, the elementary wire of 1mm was subjected to the same heat treatment as the above, which was measured for tensile strength, torsion value and fatigue strength. The results are shown in Table 1.

As a comparative example, the bare wire of 1mm ϕ formed by drawing the above raw wire of 3.5mm ϕ , and the polyester coating elementary (color tone: red) wire was tested in the same manner as the above. The polyester coating elementary wire was formed by drawing the patented steel wire of 3.5mm ϕ to a diameter of 1mm ϕ and dipping it in a solution formed by diluting polyester paint by thinner, followed

Table 1

Material	Plating thickness (μm)			Zn in plating after heating (%)	Wire diameter (mm)	Tensile strength (N/mm²)	Torsion test		Fatigue strength (N/mm²)	Rusting time in salt spray (hr)	Remarks
	Total	Cu	Zn				Torsion value	Fracture surface			
Hard steel wire (SWC)	2	2	0	0	1.0	2120	25	good	580	10	Comparative Example
	2	1.9	0.1	5	1.0	2100	22	good	570	12	Working Example
	2	1.4	0.6	30	1.0	2110	22	good	570	25	
	2	1.1	0.9	45	1.0	2090	28	good	565	35	
	2	1.0	1.0	50	1.0	2090	24	good	570	39	Comparative Example
	25	25	0	0	1.0	2070	27	good	560	25	
	25	23.75	1.25	5	1.0	2040	24	good	560	27	Comparative Example
	25	17.5	7.5	30	1.0	2060	24	good	570	55	
	25	13.75	11.25	45	1.0	2060	25	good	560	60	
	25	12.5	12.5	50	1.0	2040	25	good	565	60	Working Example
	30	30	0	0	1.0	2030	23	good	400	30	
	30	28.5	1.5	5	1.0	2010	26	good	420	32	Comparative Example
	30	21.0	9.0	30	1.0	2000	27	good	400	55	
	30	16.5	13.5	45	1.0	2010	26	good	410	65	
	30	15.0	15.0	50	1.0	2040	26	good	420	65	Working Example
Bare wire	-	-	-	※2	1.0	2170	24	good	590	5	
※1	-	-	-	※2	1.2	2160	27	good	585	※3	

(Note) ※1 ··· polyester coat wire ※2 ··· no heating ※3 ··· no rust after 300 hr

by baking by a two-bake/two-coat system. The results are shown in Table 1.

Example 2

A stainless steel wire for a spring is subjected to bright annealing to be softened, to thus form a raw wire of 2.5mm ϕ . The raw wire was applied with two-layer plating and drawn in the same manner as in Example 1, to thus obtain an elementary wire within a strength level equivalent to 1mm ϕ of JIS 3521 hard drawn steel wire SWC. The elementary wire of 1mm ϕ was formed into a coil spring and heated, which was subjected to the same test as in Example 1.
Also, as a comparative example, the bare elementary wire of 1mm ϕ formed by drawing the raw wire of 2.5mm ϕ was tested. The results are shown in Table 2.

As is apparent from Tables 1 and 2, with the plating thickness ranging from 2 to 25μm, either of the tensile strength, torsion value characteristic, fatigue strength or corrosion resistance is preferable as an elementary wire for a spring. Meanwhile, with the plating layer thickness of 30μm, the fatigue strength is significantly reduced, thus not being put in practical use. The polyester coating elementary wire is excellent in corrosion resistance.

Example 3

In the elementary wire as shown in Example 1, the whole plating thickness after drawing was set to be 5μm in place of 2μm. It was formed into a coil spring, followed by heating, and was examined for a colored state. Incidentally, similarly to Example 1, the thickness ratio of Zn in the alloy

Table 2

Material	Plating thickness (μm) Total	Cu	Zn	Zn in plating after heating (%)	Wire diameter (mm)	Tensile strength (N/mm²)	Torsion Test: Torsion value	Fracture surface	Fatigue strength (N/mm²)	Rusting time in salt spray(hr)	Remarks
Stainless steel wire for spring (WPB)	2	2	0	0	1.0	1970	12	good	310	200	Comparative Example
	2	1.9	0.1	5	1.0	1960	10	good	300	200	Working Example
	2	1.4	0.6	30	1.0	1950	8	good	315	220	
	2	1.1	0.9	45	1.0	1960	9	good	300	225	
	2	1.0	1.0	50	1.0	1960	10	good	310	230	Comparative Example
	25	25	0	0	1.0	1940	10	good	290	210	
	25	23.75	1.25	5	1.0	1940	12	good	290	220	Working Example
	25	17.5	7.5	30	1.0	1930	10	good	295	240	
	25	13.75	11.25	45	1.0	1920	8	good	290	250	
	25	12.5	12.5	50	1.0	1940	7	good	300	250	Comparative Example
	30	30	0	0	1.0	1910	6	good	180	218	
	30	28.5	1.5	5	1.0	1900	12	good	195	220	Working Example
	30	21.0	9.0	30	1.0	1900	10	good	190	240	
	30	16.5	13.5	45	1.0	1910	11	good	190	250	
	30	15.0	15.0	50	1.0	1920	12	good	180	250	Comparative Example
Bare wire	-	-	-	-	1.0	1970	10	good	310	190	

plating layer was made at 0,5,30,45, and 50%. As is apparent from Table 3, when the plating thickness ratio of Zn layer in two-layer plating is adjusted to the extent that the Zn content in the alloy plating layer is within the range of 5-45%, the color tone is significantly changed by the heat treatment, and consequently, by the use of this color change, it is possible to certainly distinguish the spring steel formed products.
Also, the present invention is superior to that with the resin coating because the resin coating is suffered

from the surface deterioration such as galling in forming, decoloration and fusing. In addition, in the case of the coil spring in Example 2, (elementary wire: stainless steel wire), when the plating thickness ratio of Zn layer in the two layer plating was adjusted to the extent that the Zn content was within the range from 2 to 45% similarly to the above, the color tone was similarly changed.

The present invention is not limited to the coil spring; but may be applied for a spring material that requires a low temperature annealing after forming (forming material, torsional spring and sheet spring and the like) or the material similar thereto.

Example 4

A hard drawn steel wire containing 0.82% C was subjected to lead patenting, pickling and descaling to thus form a raw wire of 3.5mm ϕ . The raw wire was applied with three-layer plating of a low layer of Ni, an intermediate layer of Cu and an upper layer of Zn using a three-bath continuous electro-plating bath. In this case, Ni plating was applied under the following condition: bath composition is nickel sulfamic acid: 450g/l, nickel chloride: 15g/l and boric acid: 30g/l; pH is 4; temperature is 50 °C ; and plating current density is 8A/dm^2.
Cu-plating was applied under the following condition: bath composition is $CuSO_4$:130g/l and 62%H_2SO_4 : 33cc/l solution; pH is 1.5; temperature is 30 °C ; plating current density is 5A/dm^2 ; and anode is Cu plate.
Zn plating was applied under the following condition: bath composition is $ZnSO_4 \cdot 7H_2O$: 410g/l, $AlCl_3 \cdot H$ O: 20g/l, and Na_2SO_4: 75g/l solution; pH is 4; current density is 5A/dm^2 ; and anode is Zn plate.
The plating times were set at the five kinds for changing the Zn-layer thickness ratio to the total thickness of Cu-layer and Zn-layer: namely, 0, 5, 10, 45, and 50%. At the same time, the total plating thickness of Ni-plating layer, Cu-layer and Zn-layer was adjusted to become 0, 1, 2, 5, 25 and 30μm after drawing.

After being applied with three-layer plating, the raw wire was drawn 8 times in the usual manner at a reduction ratio of 91.7% to a diameter of 1mm ϕ,
to thus obtain an elementary wire within a strength level equivalent to 1mm ϕ of JIS 3521 hard drawn steel wire SWC.
The elementary wire of 1mm ϕ was formed into tight springs having an outside diameter of 12mm, length of 20mm and a number of winding of 20. Each tight spring was heated under a condition of 150 °C × 7 min., 200 °C × 5 min., 250 °C × 4 min., 300 °C × 3.5 min., and 400 °C × 2 min., which was examined for the colored state.
Each tight spring after being heated was cooled and was examined for corrosion resistance by a salt spray test. Also, the elementary wire of 1mm ϕ was subjected to the same heat treatment as the above, which was measured for tensile strength, torsion value and fatigue strength. The results are shown in Tables 4 to 6.

As a comparative example, the bare wire of 1mm ϕ formed by drawing the above raw wire of 3.5mm ϕ , and the polyester coating elementary (color tone: red) wire was tested in the same manner as the above. The polyester coating elementary wire was formed by drawing the patented steel wire of 3.5mm ϕ to a diameter of 1mm ϕ and dipping it in a solution formed by diluting polyester paint by thinner, followed by baking by a two-bake/two-coat system. The results are shown in Table 3.

As is apparent form Tables 4 and 6, in the tight spring after heating, with the thickness of a lower Ni-layer being 2μm or more and the thickness of the Cu-Zn alloy layer being 2μm or more, all of the tensile strength, torsion value characteristic, fatigue strength and corrosion resistance are preferable as an elementary wire for a spring. Also, this tight spring exhibits excellent corrosion resistance at a thinner thickness of the Cu-Zn alloy plating layer as compared with that having the Cu-Zn alloy plating layer without the lower Ni-plating layer. Meanwhile, when the thickness of the lower Ni-plating layer exceeds 30μm and the thickness of the Cu-Zn alloy plating layer exceeds 25μm, the corrosion

Table 3

Class	Plating thickness before heating (μm)			Heating condition		Zn in plating after heating (%)	Color tone		Surface
	Total	Cu	Zn	°C	min.		before heating	after heating	
Comparative Example	5	5	0	150	7	0	red	red	Good (galling, discoloration, fusing: absence)
	5	5	0	200	5	0	red	red	
	5	5	0	250	4	0	red	red	
	5	5	0	300	3.5	0	red	red	
	5	5	0	400	2	0	red	red	
	5	4.75	0.25	150	7	5	white	white	
	5	4.75	0.25	200	5	5	white	white	
Working Example	5	4.75	0.25	250	4	5	white	gold	
	5	4.75	0.25	300	3.5	5	white	gold	
	5	4.75	0.25	400	2	5	white	gold	
Comparative Example	5	3.50	1.50	150	7	30	white	white	
	5	3.50	1.50	200	5	30	white	white	
Working Example	5	3.50	1.50	250	4	30	white	gold	
	5	3.50	1.50	300	3.5	30	white	gold	
	5	3.50	1.50	400	2	30	white	gold	
Comparative Example	5	2.75	2.25	150	7	45	white	white	
	5	2.75	2.25	200	5	45	white	white	
Working Example	5	2.75	2.25	250	4	45	white	gold	
	5	2.75	2.25	300	3.5	45	white	gold	
	5	2.75	2.25	400	2	45	white	gold	
Comparative Example	5	2.50	2.50	150	7	50	white	white	
	5	2.50	2.50	200	5	50	white	white	
	5	2.50	2.50	250	4	50	white	white	
	5	2.50	2.50	300	3.5	50	white	white	
	5	2.50	2.50	400	2	50	white	white	
*1	100	-	-	200	5	-	red	muddy red	*2

(Note). *1 ··· comparative example (polyester coat)
*2 ··· galling, discoloration, fusing: presence

Table 4

Spring steel material	Plating thickness (μm)				Zn in Cu-Zn alloy plating after heating (%)	Wire diameter (mm)	Tensile strength (N/mm²)	Torsion Test		Rusting time in salt spray (hr)	Remarks
		Ni	Cu	Zn				Torsion value	Fracture surface		
Hard steel wire (SWC)	1	0	1.0	0	0	1.0	2130	25	good	4	Comparative Example
	1	0	0.95	0.05	5	1.0	2110	26	good	7	
	1	0	0.90	0.10	10	1.0	2110	25	good	6	
	1	0	0.55	0.45	45	1.0	2080	25	good	7	
	1	0	0.5	0.5	50	1.0	2100	25	good	12	
	2	1	1.0	0	0	1.0	2100	24	good	4	Comparative Example
	2	1	0.95	0.05	5	1.0	2080	26	good	6	
	2	1	0.90	0.10	10	1.0	2070	26	good	6	
	2	1	0.55	0.45	45	1.0	2100	27	good	7	
	2	1	0.5	0.5	50	1.0	2100	24	good	10	Working Example
	4	0	3.6	0.4	10	1.0	2120	25	good	14	
	4	2	1.90	0.1	5	1.0	2100	25	good	16	
	4	2	1.80	0.2	10	1.0	2040	23	good	18	
	4	2	1.10	0.90	45	1.0	2050	21	good	48	
	4	2	1.0	1.0	50	1.0	2100	26	good	50	

Table 5

Spring steel material	Plating thickness (μm)				Zn in Cu-Zn alloy plating after heating (%)	Wire diameter (mm)	Tensile strength (N/mm^2)	Torsion Test		Rusting time in salt spray(hr)	Remarks
	Total	Ni	Cu	Zn				Torsion value	Fracture surface		
Hard steel wire (SWC)	10	0	7	0	30	1.0	2100	25	good	40	Working Example
	10	5	4.75	0.25	5	1.0	2120	21	good	28	
	10	5	4.50	0.50	10	1.0	2080	23	good	32	
	10	5	2.75	2.25	45	1.0	2060	23	good	75	
	10	5	2.5	2.5	50	1.0	2090	22	good	80	
	55	0	38.5	16.5	30	1.0	2040	26	good	60	
	55	30	23.75	1.25	5	1.0	2040	27	good	50	
	55	30	22.5	2.5	10	1.0	2030	24	good	55	
	55	30	13.75	11.25	45	1.0	2040	24	good	95	
	55	30	12.5	12.5	50	1.0	2040	24	good	100	

Table 6

Spring steel material	Plating thickness (µm)				Zn in Cu-Zn alloy plating after heating (%)	Wire diameter (mm)	Tensile strength (N/mm²)	Torsion Test		Rusting time in salt spray (hr)	Remarks
	Total	Ni	Cu	Zn				Torsion value	Fracture surface		
Hard steel wire (SWC)	75	0	52.5	22.5	30	1.0	2010	26	good	75	Working Example
	75	40	33.25	1.75	5	1.0	2010	25	good	60	
	75	40	31.5	3.50	10	1.0	2030	25	good	65	
	75	40	19.25	15.75	45	1.0	2010	26	good	100	
	75	40	17.5	17.5	50	1.0	2010	26	good	105	
Bare wire	-	-	-	-	-	1.0	2160	24	good	0.5	Comparative Example
※1	-	-	-	-	-	1.2	2160	27	good	※2	

(Note) ※1 ··· polyester coat wire ※2 ··· no rust after 300 hr

resistance is not improved in proportion to the increase in the thickness.

Example 5

In the elementary wire of 1mm ϕ as shown in Example 4, the whole plating thickness after drawing was set to be 4μm and the thickness ratio of the Zn-layer to the total thickness of the Cu-layer and the Zn layer

is changed to 0, 5, 10, 45, and 50%. Each wire was formed into a coil spring, followed by heating, and was examined for a colored state. The results are shown in Table 7 along with the manufacturing conditions such as the plating layer thickness and heating condition. As is apparent from Table 7, when the thickness ratio of the Zn-layer is selected as 10 to 45%, the Zn content in the Cu-Zn alloy plating layer after heat treatment becomes 10 to 45%. Thus, by the heat treatment with the condition of 250°C × 4 min. or more to 400°C × 2 min. or more, the color tone is changed into gold, which makes it possible to certainly distinguish the spring steel formed products. Further, the present invention is superior to that with the resin coating because the resin coating is suffered from the surface deterioration such as galling in forming, decoloration and fusing.

The present invention is not limited to the coil spring; but may be applied for a spring material that requires a low temperature annealing after forming (forming material, torsion spring and sheet spring and the like) or the material similar thereto.

Table 7

Class	Plating thickness before heating (μm)				Heating condition		Zn in Cu-Zn alloy plating (%)	Color tone		Surface
		Ni	Cu	Zn	°C	min.		before heating	after heating	
Comparative Example	4	0	4	0	150	7	0	red	dark red	Good (galling, discoloration, fusing: absence)
	4	0	4	0	200	5	0	red	dark red	
	4	0	4	0	250	4	0	red	dark red	
	4	0	4	0	300	3.5	0	red	dark red	
	4	0	4	0	400	2	0	red	dark red	
Comparative Example	4	2	1.90	0.10	150	7	5	white	white	
	4	2	1.90	0.10	200	5	5	white	white	
	4	2	1.90	0.10	250	4	5	white	white	
	4	2	1.90	0.10	300	3.5	5	white	white	
	4	2	1.90	0.10	400	2	5	white	white	
	4	2	1.80	0.20	150	7	10	white	white	
	4	2	1.80	0.20	200	5	10	white	white	
Working Example	4	2	1.80	0.20	250	4	10	white	gold	
	4	2	1.80	0.20	300	3.5	10	white	gold	
	4	2	1.80	0.20	400	2	10	white	gold	
Comparative Example	4	2	1.10	0.90	150	7	45	white	white	
	4	2	1.10	0.90	200	5	45	white	white	
Working Example	4	2	1.10	0.90	250	4	45	white	gold	
	4	2	1.10	0.90	300	3.5	45	white	gold	
	4	2	1.10	0.90	400	2	45	white	gold	
Comparative Example	4	2	1.0	1.0	150	7	50	white	white	
	4	2	1.0	1.0	200	5	50	white	white	
	4	2	1.0	1.0	250	4	50	white	white	
	4	2	1.0	1.0	300	3.5	50	white	white	
	4	2	1.0	1.0	400	2	50	white	white	
*1			-	-	200	5	-	red	dark red	*2

(Note) *1 ··· polyester coat
*2 ··· galling, discoloration, fusing: presence

Claims

1. A color-developing metal product for spring plated on the surface with alternate layers of Cu and Zn to be alloyed by a low temperature thermal diffusion after spring-forming.

2. A color-developing metal product for spring according to claim 1, wherein said plating layer is formed of a 5-45%Zn and remaining Cu .

3. A color-developing metal product for spring according to claim 1 or 2, wherein a thickness of said plating layer is within the range from 2 to 25µm.

4. A color-developing metal product for spring according to claim 1 or 3, wherein said plating layer is formed of a 10-45%Zn and the remaining Cu exhibiting a color tone of gold after alloying.

5. A color-developing metal product for spring according to claim 1 or 3, wherein said plating layer is formed of a 5-10% Zn and the remaining Cu exhibiting a color tone of red copper after alloying.

6. A method of using a color-developing plated metal product for spring comprising the steps of: applying two-layer plating of a lower layer of Cu and an upper layer of Zn on the surface of a spring steel material to the extent that the thickness ratio of a Zn layer to the whole thickness of the plating layer is within the range from 5 to 45%; adjusting a final plating thickness of said plated spring to 2-25µm and spring-forming it; heating the spring-formed spring material at 250-400 °C for low temperature annealing thereby allowing said plating layer to be colored.

7. A method of using a color-developing plated metal product according to claim 6, wherein the heating time in said low temperature annealing is set to a time (t) satisfying the following equation (1).

$$\log t \gtrsim 1.193 - 2.386 \times 10^{-3} T \quad (1)$$

wherein T indicates a heating temperature (°C) in a low temperature annealing, and (t) is a heating time (min.).

8. A method of using a color-developing plated metal product for spring according to claim 6 or 7, wherein either of a hard drawn steel wire, piano wire or a spring stainless steel wire is used as said spring steel material.

9. A color-developing plated metal product formed of spring steel comprising a Ni plating layer on the surface of a spring steel material, and alternate layer of Cu and Zn to be alloyed by heating diffusion in low temperatures after spring-forming formed on said Ni-plating layer.

10. A color-developing plated metal product according to claim 9, wherein said alternate layers of Cu and Zn are composed of a 5-45%Zn and the remaining Cu exhibiting a color tone of gold after alloying .

11. A color-developing plated metal product according to claim 9 or 10, wherein a thickness of said Ni plating layer is within the range of 2-30µm and total thickness of said alternate layers of Cu and Zn is within the range of 2-25µm.

12. A color-developing plated metal product according to claim 9 or 11, wherein said alternate plating layers of Cu and Zn comprise 10-45%Zn and the remaining Cu, exhibiting a color tone of gold after alloying.

13. A color-developing plated metal product according to claim 9 or 11 wherein said alternate plating layers of Cu and Zn comprise 5-10%Zn and the remaining Cu, exhibiting a color tone of red copper after alloying.

14. A method of using a color-developing plated metal product for spring comprising the steps of: applying three-layer plating of a lower layer of Ni, an intermediate layer of Cu and an upper layer of Zn on the surface of a spring steel material to the extent that the thickness ratio of a Zn layer to the total

thickness of said Cu layer and said Zn layer is within the range from 10 to 45%; adjusting a plating thickness of said Ni layer to 2-30μm and the total thickness of said Cu layer and said Zn layer to 2-25μm and spring-forming it; heating the spring-formed spring material at 250-400 °C for low temperature annealing thereby allowing said plating layer to be colored.

15. A method of using a color-developing plated metal product for spring according to claim 14, wherein the heating time in said low temperature annealing is set to a time (t) satisfying the following equation (1),

$$\log t \geq 1.193 - 2.386 \times 10^{-3}\, T \qquad (1)$$

wherein T indicates a heating temperature (°C) in a low temperature annealing, and (t) is a heating time (min.).

16. A method of using a color-developing plated metal product according to claim 14 or 15, wherein either of a hard drawn steel wire, piano wire or a spring stainless steel wire is used as said spring material.

F I G. 1

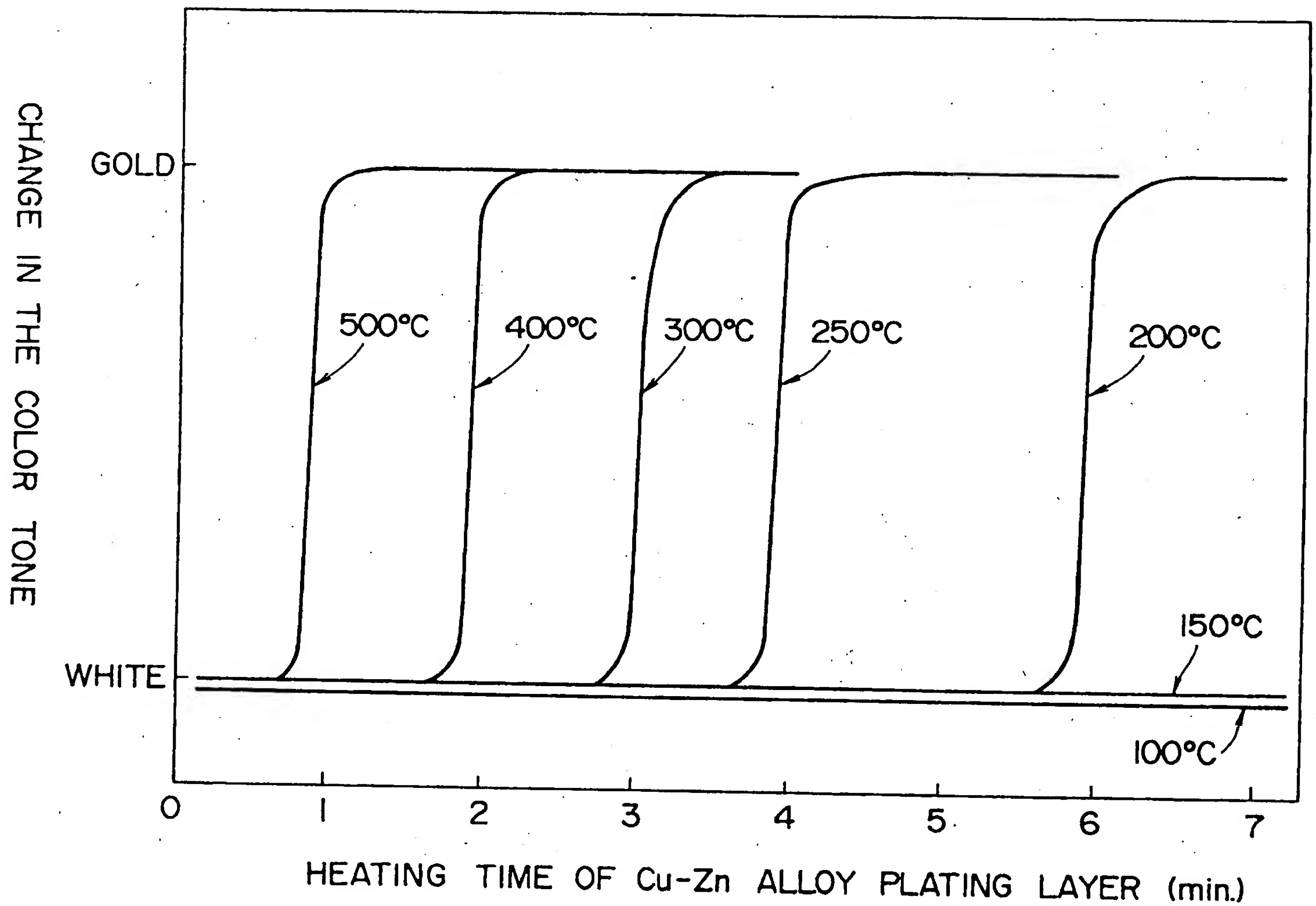
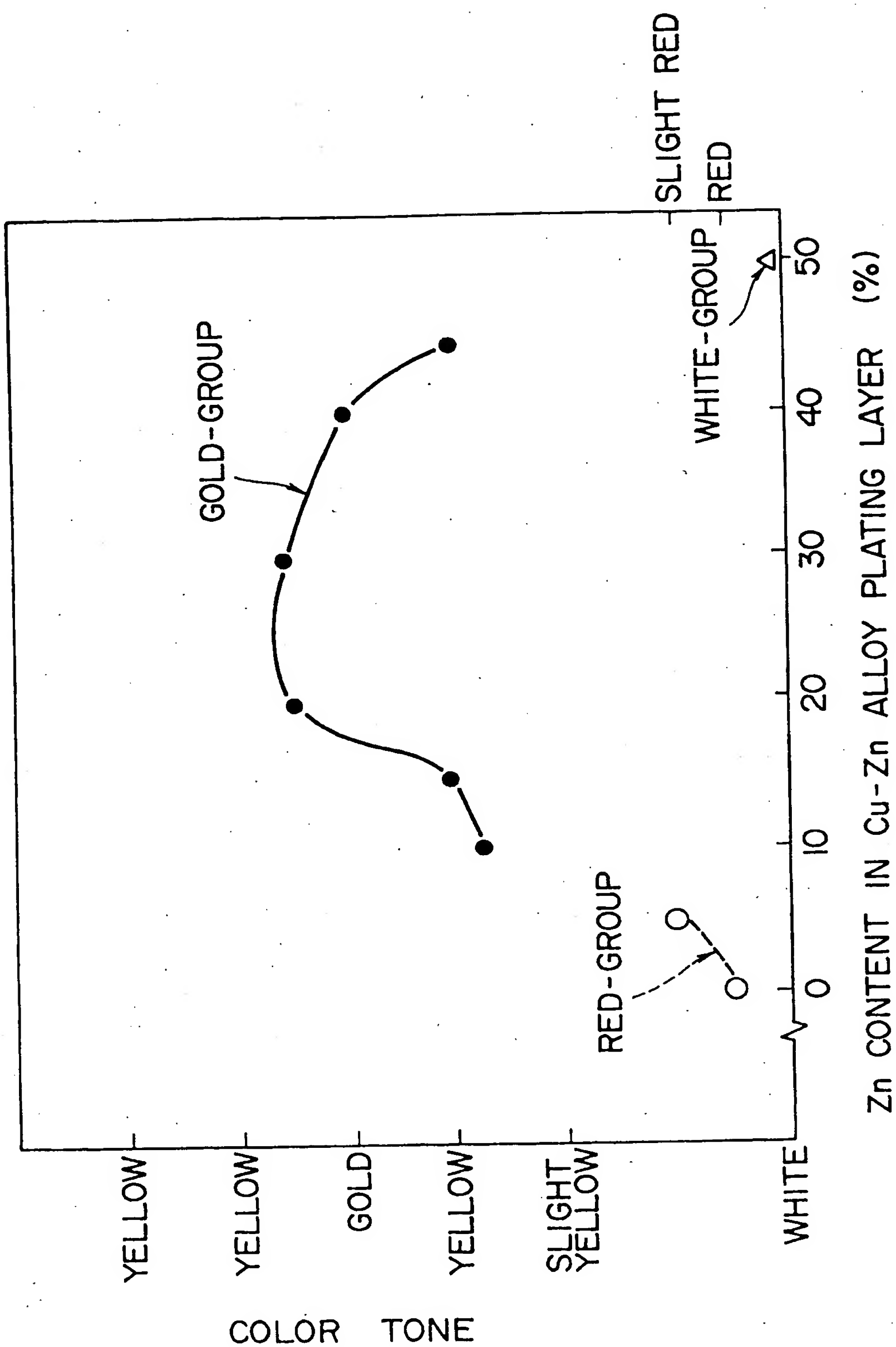

CHANGE IN THE COLOR TONE
GOLD
WHITE
500°C
400°C
300°C
250°C
200°C
150°C
100°C
0
1
2
3
4
5
6
7
HEATING TIME OF Cu-Zn ALLOY PLATING LAYER (min.)

FIG. 2


GOLD-GROUP
RED-GROUP
WHITE-GROUP
SLIGHT RED
RED
YELLOW
YELLOW
GOLD
YELLOW
SLIGHT YELLOW
WHITE
COLOR TONE
0
10
20
30
40
50
Zn CONTENT IN Cu-Zn ALLOY PLATING LAYER (%)

F I G. 3

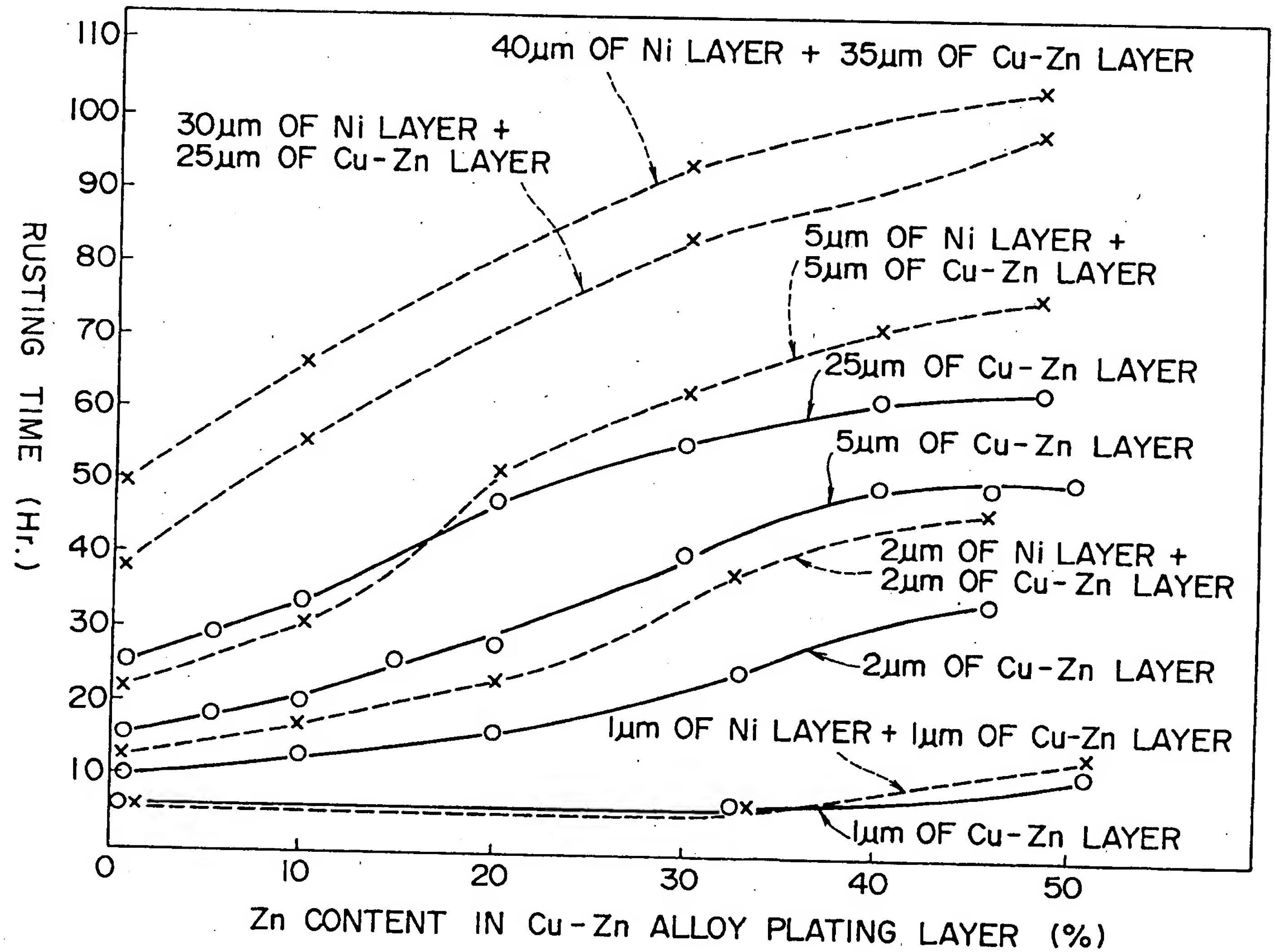
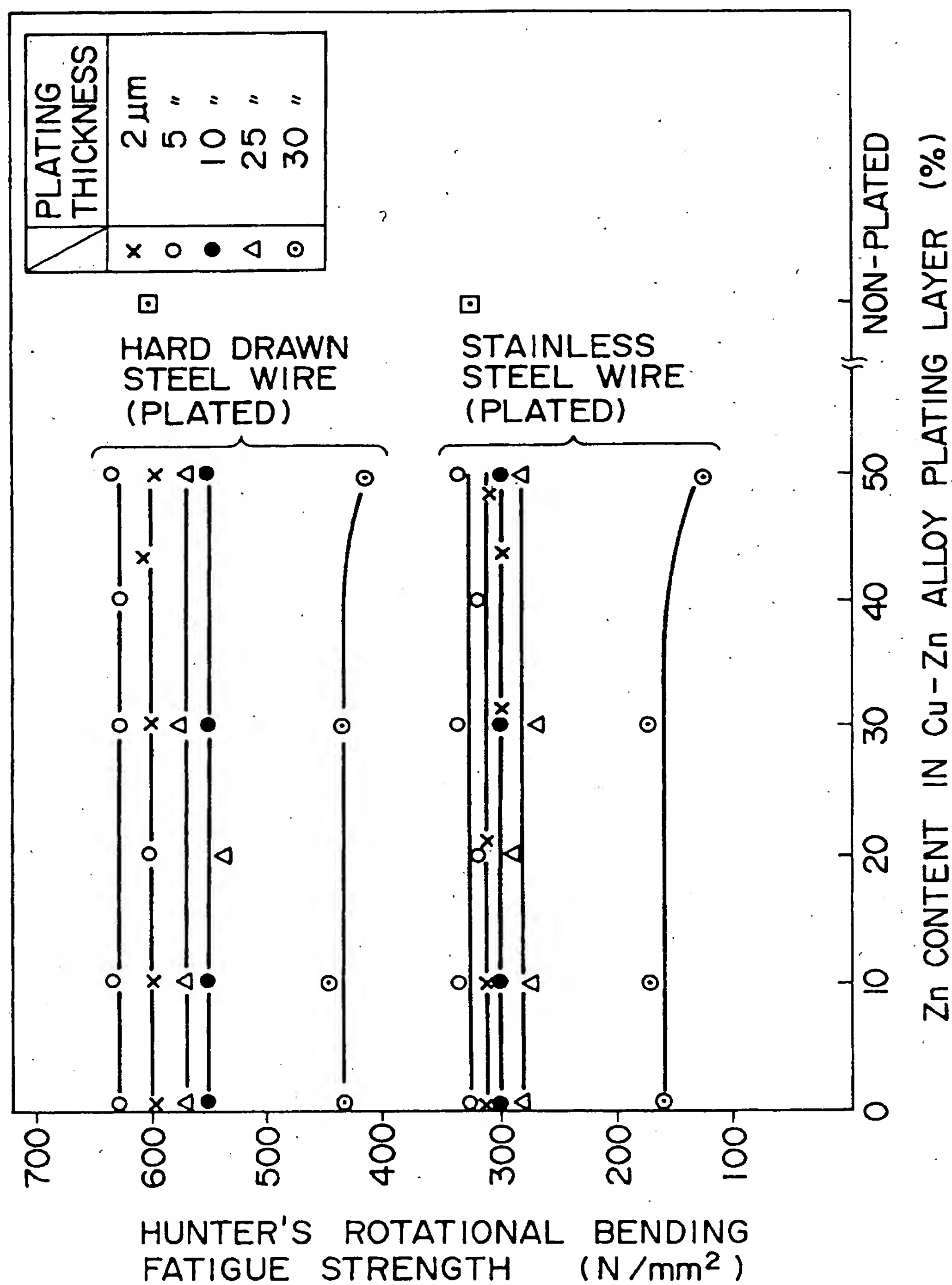

40μm OF Ni LAYER + 35μm OF Cu-Zn LAYER
30μm OF Ni LAYER +
25μm OF Cu-Zn LAYER
5μm OF Ni LAYER +
5μm OF Cu-Zn LAYER
25μm OF Cu-Zn LAYER
5μm OF Cu-Zn LAYER
2μm OF Ni LAYER +
2μm OF Cu-Zn LAYER
2μm OF Cu-Zn LAYER
1μm OF Ni LAYER + 1μm OF Cu-Zn LAYER
1μm OF Cu-Zn LAYER
RUSTING TIME (Hr.)
Zn CONTENT IN Cu-Zn ALLOY PLATING LAYER (%)
0
10
20
30
40
50
60
70
80
90
100
110

FIG. 4


PLATING THICKNESS
× 2 μm
○ 5 〃
● 10 〃
△ 25 〃
⊙ 30 〃
HARD DRAWN STEEL WIRE (PLATED)
STAINLESS STEEL WIRE (PLATED)
NON-PLATED
0
10
20
30
40
50
Zn CONTENT IN Cu-Zn ALLOY PLATING LAYER (%)
700
600
500
400
300
200
100
HUNTER'S ROTATIONAL BENDING FATIGUE STRENGTH (N/mm²)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 5424

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-2 115 749 (MICHAEL M. RUBIN) *whole document* ---	1-6	C23C26/00 C23C28/02 C25D5/50
A	US-A-3 762 883 (GEORGE A. SHEPARD) * column 3, line 28 - line 45 * * column 10, line 10 - line 21 * ---	1,6	
A	CHEMICAL ABSTRACTS, vol. 96, no. 6, February 1982, Columbus, Ohio, US; abstract no. 39207e, NISSHIN STEEL 'brass coatings on steel sheets' page 259 ;column 96 ; * abstract * & jp8196068 (03-09-81) ---	3,6	
A	FR-A-2 478 131 (IRCA SPA INDUSTRIA RESISTENZE CORAZZATE ED AFFINI) ---		
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 248 (C-843)25 June 1991 & JP-A-30 79 790 (SUMITOMO ELECTRIC IND) 4 April 1991 * abstract * ---		TECHNICAL FIELDS SEARCHED (Int. Cl.5) C23C C25D
A	Derwent Publications Ltd., London, GB; AN 89-251938 C35 & JP-A-1 182 669 (NISSHIN STEEL) 20 July 1989 * abstract * -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 MAY 1993	ELSEN D.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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